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(71) Applicant: W.R. GRACE & CO.-CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036 (US).

(72) Inventors: MURRAY, Thomas, J. ; 145 Fruit Street, Mansfield, MA 02048 (US). TESSIER, Noel, J. ; 162 Landry Avenue, North Attleboro, MA 02760 (US).

(74) Agents: TRIANO, Nicholas, P., III et al.; W.R. Grace & Co.-Conn., 55 Hayden Avenue, Lexington, MA 02173 (US).

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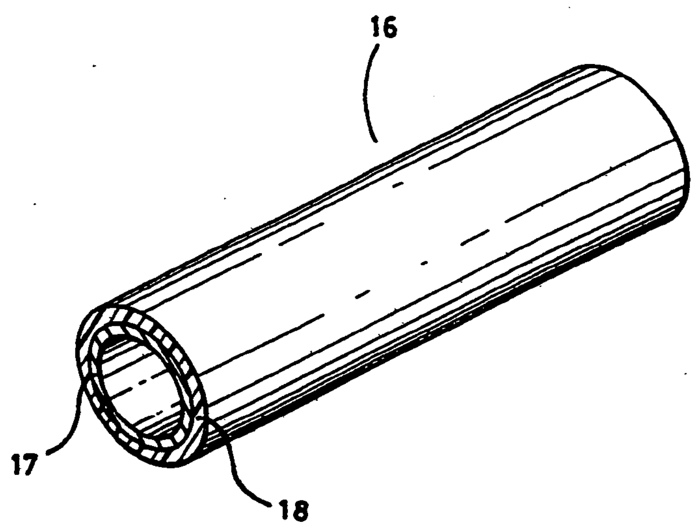

(57) Abstract

Flexible syntactic foam insulation, and methods for making it, are disclosed. A low melt index thermoplastic resin is fluidified to produce a melt stream, and microspheres are metered into the melt stream under low shear conditions. The method allows for faster production of syntactic foams and for the production of higher quality foams because breakage of the microspheres is substantially reduced. An integral insulated pipe section (16) including a pipe (17) and a covering of syntactic foam insulation (18) is produced.

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THERMOPLASTIC SYNTACTIC FOAM PIPE INSULATION

FIELD OF THE INVENTION

This invention relates generally to syntactic foam insulation, and more particularly to flexible thermoplastic syntactic foam pipe insulating material made by fluidifying a thermoplastic resin having a defined melt index to produce a melt stream; metering a spherical filler into the melt stream under low shear conditions to form a mixture, and forming the mixture into a final form.

BACKGROUND OF THE INVENTION

Off-shore petroleum production requires the use of submarine pipes or conduits to transport oil or gas back to a centralized surface platform or to shore. In some fields, the oil or gas contains paraffins that can precipitate out as the temperature of the oil or gas passing through the pipes is lowered due to heat transfer from the pipe contents to the cold ocean. This significantly reduces flow or causes blockage of production lines, increasing the cost of production. If blockage occurs costly mechanical or chemical means are necessary to clear any blockage. Added expenses are the cost of shutting down production and the potential loss of any pipe contents caused during removal of the blockage.

Several techniques are known for alleviating this problem: 1) adding chemicals to the oil to prevent paraffin precipitation, 2) heating the production lines, or 3) insulating the pipes. However, adding chemicals to the oil or gas is costly because of the effort and money expended in purchase and addition, and the chemicals must later be refined out of the oil. Heating the pipeline is also costly because it is not energy-efficient and requires heating equipment which must be installed over kilometers of pipeline, and monitored for proper operation. On the other hand, insulating the production lines is a cost-effective

solution because the insulation may be installed on the pipeline before it is laid and needs no continuous monitoring.

Submarine oil or gas production pipelines must also be physically protected. Steel pipes are most commonly used in fabricating off-shore pipelines, and as such require protection from the corrosive sea water. Typically neoprene or epoxy coatings are used for this purpose. However, such coatings are subject to abrasion caused by the installation process, and an additional overcoating is needed, e.g., of polyethylene.

Appropriate syntactic foam insulation could insulate the pipe as well as provide corrosion resistance, abrasion resistance and resistance to hydrostatic pressures. Syntactic materials are those in which hollow spherical filler material is embedded in a polymeric matrix. The filler material, most often glass or plastic microspheres in the micron size range, imparts thermally-insulative properties to the syntactic material; generally, for a given thickness of syntactic material, as the concentration of microspheres in the matrix rises, so does the insulative property of the syntactic material.

Additional physical attributes such as increased resilience, low thermal conductivity, low creep, and flexibility or elasticity may be given to the syntactic material through the selection of various polymeric matrices. For instance, it has long been desired to make a flexible syntactic foam insulation which could be formed directly on the pipe sections, or wrapped around it as a sleeve or a self-adhesive tape, before the pipe is shipped to a lay barge for pipe laying. This "pre-coating" is desirable because it means the crew laying the pipe now has one less task to do, namely coating the pipe sections, although the joints must still be wrapped and sealed. Also, the flexibility is necessary because the pipe sections must flex and bend during installation. For example, in the commonly-used "j-curve" pipe-laying method, pipe sections are welded together on a lay barge moving horizontally, while the pipeline is lowered down to the ocean floor, typically entering the water at an angle of from about 60 to 80° from the horizontal. As the long pipeline reaches the ocean floor, it forms a "J" shape as it bends. Conventional syntactic foams, made of thermoset resins, are not flexible enough for such an application. Thus, it would be advantageous to select a polymeric base for the syntactic foam which is flexible enough for such an application, such as several of the thermoplastic resins.

A drawback with existing syntactic foam insulating materials, however, is the relative difficulty of making them easily and quickly in large quantities, such as for coating long sections of pipe, and also of the desired quality. Currently

available syntactic foams are made using thermoset resins such as polyurethane; these resins are more difficult to work with than thermoplastic resins because they may only be processed at temperatures below the B-stage of the resin, i.e., the temperature at which the resin begins to cross-link. Further, such foams do not have the desired flexibility to bend with the pipe during installation, and also often absorb water, requiring a separate coating to make the foam water-impermeable.

Syntactic foam insulation having a thermoplastic matrix has been long desired, but hard to make. Particularly, it is difficult to compound glass microspheres and other hollow spherical fillers into a thermoplastic polymeric matrix at low enough shear forces to prevent crushing the spheres during the process. The thermal conductivity of an effective submarine pipe insulation needs to be less than about 0.15 W/m-°K. When about 5% or greater of the spheres in the matrix are crushed, it is difficult to attain this necessary level of thermal conductivity. Furthermore, the structural properties of the syntactic foam are also adversely affected.

One method towards this end is taught in European Patent Application 473 215 A1, wherein microspheres that have been treated with a chain scission agent are added to a fluid stream of short chain polypropylene or polybutylene to form a crosslinked syntactic foam insulative material. This method is taught as useful for producing material of a low thermal conductivity. However, the plastic starting materials taught for use therein are generally not optimum for submarine pipe insulation, because while the short chain polypropylene or polybutylene affords low breakage of the microspheres, the method requires the presence of a chain scission agent, coated on the microspheres, to cross-link the short-chain polymer. Without the presence of this agent, the finished insulation would be totally unacceptable for use as submarine pipe insulation, because it would not be hydrostatic pressure-resistant, abuse-resistant, or creep-resistant. Furthermore, the chain-scission agent stiffens the plastic matrix, decreasing the flexibility of the material so as to make it impractical for use as submarine pipe insulation, because it will not flex well as the pipe is laid.

Buoyant thermoplastic syntactic cable jacketing has been made, but such jacketing contains a large amount of entrained air to keep the cable jacketing buoyant. Such materials are inappropriate for insulating deep sea pipeline, however; the air pockets in the material will cause the material to collapse at ocean-floor pressures, leading to absorption of water in the interstices of the material. These materials are also not abrasion or heat resistant, and cannot be

made desirably thin to bend with the pipe, while providing efficient insulation for it.

The inventors have thus found no truly satisfactory way to compound spherical fillers into a thermoplastic polymeric matrix to make an advantageously thin, flexible syntactic foam pipe insulating material without 1) crushing a substantial proportion of the spherical filler during processing, 2) being time-consuming and difficult to put into practice on a large scale, or 3) utilizing specialized, or heavily modified standard equipment.

Thus it is an object of the invention to provide a method for making syntactic foam insulation having superior thermal and structural qualities which may be carried out on a large scale, e.g., in sufficient volume for pipe applications, on presently available equipment.

It is another object of the invention to provide a method for making one-piece pipe units ready for assembly in submarine oil or gas conduits which comprise a layer of flexible syntactic foam insulation on the pipe's outer surface.

It is a further object of the invention to provide one-piece insulated pipe units ready for assembly in submarine oil or gas conduits made by the above method.

It is yet another object of the invention to provide adhesive flexible syntactic foam insulating tapes and sleeves made by the method of the invention.

Further objects of the invention are to provide a syntactic foam insulation made by a method of the invention, and to provide a method of insulating pipe utilizing a syntactic foam made by a method of the invention.

Other objects of the invention will be apparent to those of ordinary skill in the art upon reading the specification, claims and drawings.

SUMMARY OF THE INVENTION

The present invention relates to a method of making syntactic foam insulation, comprising the steps of fluidifying a thermoplastic resin having a melt index of from 3 to 30g/10 min to produce a melt stream; metering a spherical filler into the melt stream under low shear conditions to form a mixture, and forming the mixture into a final form. The invention further relates to syntactic foam insulation made by the above process.

DESCRIPTION OF THE DRAWINGS

Figure 1 depicts in simplified side view a double-stage extruder carrying out the method of the invention.

Figure 2 depicts in partial cross-section a ready-to-use pipe section in accordance comprising an outer sleeve of syntactic material superimposed over the outer pipe surface.

Figure 3 depicts in plan view a pipe section wrapped with a self-adhesive syntactic foam tape made in accordance with the invention.

DESCRIPTION OF THE INVENTION

The objects of the invention have been substantially accomplished by the use of a method which, in a preferred embodiment, uses a two-stage extrusion process, whereby a first stage of an extruder means fluidizes a thermoplastic resin base and conveys it to a second stage of an extruder means where, under low shear conditions, a spherical filler material is introduced into the fluid plastic stream. In this preferred embodiment the thermoplastic and filler material thereafter mix in the second stage of the extruder barrel and the fluid mixture is deaerated and extruded into a desired final form. The resulting product contains a substantially homogeneous distribution of spherical filler material in the polymeric matrix, which, as stated previously, is crucial to maximizing the thermal and structural properties of the finished syntactic foam.

"Thermoplastic", as used herein, is intended to mean any plastic, polymeric, or elastomeric base commonly used in the art as feed stock in extrusion or extrusion-related processes which can be heated and softened repeatedly without suffering any basic change in characteristics. Thermoplastics used in this invention must be of a high "melt index," which are defined as those which, under test conditions specified by ASTM standard D3835, have a low viscosity, i.e., in the range of from about 3.0 to 30g/10min, preferably from about 15 to 30g/10min, and more preferably from about 20 to 25g/10min. Thermosetting resins are inappropriate for use in the invention.

Examples of thermoplastic resins are polyimides, acrylonitrile-butadiene-styrene ("ABS") resins, acetals, acrylics, cellulosics, chlorinated polyethers, fluorocarbons, nylons (polyamides), polycarbonates, polyolefins and copolymers thereof including, but not limited to, polyethylenes and copolymers thereof, polypropylenes and copolymers thereof, chlorinated or fluorinated polyolefins and copolymers thereof; polystyrenes, and vinyls, e.g., polyvinyl chloride. The omission of any specific type of thermoplastic resin should not be construed as a limitation on the invention. It should also be noted that mixtures of one or more thermoplastic resins may be employed.

Specific types of resins within each class named above that are suitable for use in the invention are well-known to those of ordinary skill in the art and need not be mentioned here. However, the inventors have found that thermoplastic polyolefins ("TPO") such as those manufactured under the trademarks HIFAX (Himont) and FLEXOMER (Union Carbide) are particularly suitable for use in the invention, as are SURLYN (E. I. Du Pont de Nemours Co.) ionically cross-linked thermoplastic polymers derived from ethylene/methacrylic acid copolymers, and thermoplastic elastomers ("TPE") such as PEBAX (Atochem), which is a polyether blocked polyamide ("PEBA"). However, the invention should not be limited to the use of these resins. These thermoplastic resins provide the necessary flexibility to the finished syntactic foam insulation, which is also very desirable from the standpoint of producing such articles as syntactic foam insulating tapes and sleeves, which by their nature need to be flexible and/or pliable for easy installation. Although these resins are flexible, they are also resistant to creep, elongation, abrasion and corrosion, making their use in pipeline applications even more desirable. Further, such resins are very resistant to the high temperatures of the pipelines (as high as 125°C). These resins have a characteristic chain length that distinguishes them from other thermoplastic resins that have been used in this art. Specifically, these resins have longer chains and low melt indices, which makes them very flexible and strong. Fluidification of such resins and addition of spherical filler under low shear conditions to make a syntactic foam having a high proportion of intact microspheres, as described herein, makes the use of short chain polymers with a chain-scission agent, as taught in U. S. Patent No. 5,158,727, unnecessary.

The spherical filler used in the invention may be any type of hollow spheres which are typically used in making syntactic foams. (For brevity and convenience the term "microspheres" will be used hereinafter to describe spherical filler used in the invention.) The microspheres are preferably made of glass, but may also be made of plastic or other materials well-known to those skilled in the art, provided that they will not melt under the conditions necessary for fluidification of the thermoplastic resin to produce the melt stream. The size range of the spheres will depend on the particular demands to be made on the syntactic foam to be produced. Generally, the spheres will range in diameter from about 3 to 100μ, preferably from about 5 to 80μ, more preferably from about 20 to 80μ, even more preferably from about 20 to 70μ, and most preferably from about 50 to 70μ. Microspheres of more than one size, or a range of sizes, may be used, e.g., a blend of spheres ranging in diameter from about 1 to 20μ and spheres ranging in diameter from about 50 to 100μ. Thus in some applications a

such a size distribution may allow denser packing of the microspheres in the finished syntactic foam. The strength of the microspheres is critical; the pure microspheres should be able to withstand pressures of from 6.89 $\times 10^3$ to 27.6 $\times 10^3$ MpA under conditions according to ASTM D3102 while sustaining no more than 20% breakage. The density of the microspheres is preferably in the range of from about 0.1 to 1.1g/cc, and more preferably from about 0.20 to 0.40g/cc.

The method is generally carried out using extrusion apparatus, as such apparatus are widely available. Typically, a two-stage extruder like the double-screw unit depicted (in greatly simplified form) in FIG. 1 may be employed. Such extruders are advantageous because they allow addition and fluidification of the resin in the first stage, and addition of the spherical filler in the second stage, thus making separate apparatus for carrying out the fluidification and filler addition steps unnecessary. However, we think that there may be some cases where separation of the fluidification and filler addition functions are desirable or necessary, and is thus within the scope of the invention. Extruders that may be used in the method of the invention are well-known in the art; conventional double-screw extruders or double-stage Buss Kneader double-screw extruders may be used, with a corotating design being preferable.

Referring now to FIG. 1, such a two-stage extruder comprises a feed hopper 1 into which thermoplastic feed material is placed for extrusion. A feeder such as an auger feeder (not shown) may be used if more precise feed stock addition is desired. The feed material passes from hopper 1 through feed throat 2 onto screw 3, which is driven by a motor unit 6b coupled by a belt 6a to a gear reducer 5 to a thrust bearing 4 connected to screw 3. The design of screw 3 within first-stage barrel 7 is of a geometry to effectively plasticate, shear and meter the thermoplastic resin in the first-stage barrel 7 into a melt stream of the desired viscosity. Those skilled in the art will know how to fabricate such a screw.

As screw 3 rotates, the thermoplastic is pumped into first stage barrel 7, which is heated by heaters 8 monitored by thermocouples 9. The heat produced by heaters 8 and the frictional action of screw 3 against the feed material and first stage barrel 7 liquefies the thermoplastic, forming a melt stream which is metered into second stage barrel 10.

As the melt stream is metered into second stage barrel 10, microspheres 12 (which have been previously placed into microsphere hopper 11) are metered into the melt stream in second stage barrel 10 under low shear conditions; it is preferred to meter microspheres using a feeder such as a weight belt side feeder.

The precise addition rate will depend on the desired concentration of microspheres 12 in the syntactic foam, and the extrusion rate. The geometry of the section of screw 3 under microsphere hopper 11 must be chosen so the microspheres are folded gently into the melt stream; such "low shear" profile screw designs will be apparent to those skilled in the art, and such screw profiles provide the necessary low shear conditions for addition of microspheres without breakage. Thus, providing "low shear conditions" in accordance with the invention means using "low shear" designs to gently fold spherical filler into the melt stream containing the low melt index thermoplastic resins of the invention.

The microspheres 12 are thus carried into the melt stream and mixed into it with little or no breakage; less than 5% breakage is important. Preferably less than 3% of the microspheres in the thermoplastic are broken. More preferably, substantially all of the microspheres present are unbroken. The mixture is transported down second stage barrel 10, heated by heaters 13 and regulated by thermocouples 14. A venting zone 16 to allow the removal of any air entrained into the melt stream caused by the mixture of the microspheres into the melt stream is preferably installed in second stage barrel 10. It is highly desirable to have the venting zone substantially remove any unreinforced air (i.e., air not contained within microspheres) from the extrudate, because the presence of unreinforced air in the matrix of the syntactic foam insulation makes the insulation highly susceptible to water incursion and collapse at high hydrostatic pressures, resulting in a significant reduction in the insulative efficiency of the insulation.

Higher microsphere loadings impart greater insulative capacity to the syntactic foam insulation. If higher loadings of microspheres in the syntactic foam are desired, i.e., about 30-50% by volume of the foam insulation, we have found it advantageous to meter a proportion of the spherical filler into a first point of the melt stream under low shear conditions, and the remainder at a second point of the melt stream, located downstream of the first, under low shear conditions. Generally, the proportion of filler metered into the first point ranges from 10 to 90%, with 30 to 80% being preferred, and 50 to 70% particularly preferred.

Other additives may be added to the melt stream along with the spherical filler if desired, such as silanes, adhesion promoters, or coupling agents.

The mixture exits at the screw tip 15, at which point is connected a die of some kind, such as a flat sheet die, a profiled sheet die, a hollow mandrel die, etc. The mixture is then pulled, rolled, cast, chopped, etc. into the desired final

form. The final form may be spheres, pellets, tapes or ribbons, etc. We have also found pellets of the syntactic foam to be useful as a masterbatch from which other insulative articles may be made. For instance, syntactic foam pellets may be blended with, e.g., EPDM rubber or extender resin and extruded to form an insulated pipe wrap that is more elastomeric and abuse-resistant.

The resulting syntactic foam may be installed on pipe in a number of ways. An integral insulated pipe section like that depicted in partial cross-section in FIG. 2 may be made by placing a section of pipe to be insulated within a cylindrical form; the syntactic foam insulation may then be extruded into the space between the form and the pipe's outer surface to form the outer coating. Referring to FIG. 2, the resulting integral insulated pipe section 16 comprises a pipe 17 and a covering of syntactic foam insulation 18. After removal of the form the integral insulated pipe section is ready to ship to the laybarge where it may be inserted into a pipeline without any further preparation.

For covering the joint sections of pipe, an insulative tape may be wrapped around the joint. However, time is of the essence when laying pipeline, and wrapping tape over a joint is time consuming. Preferably, therefore, a custom molded clamshell-type insulative enclosure may be made by compression molding or casting the fluidified syntactic foam insulation into the desired configuration. The insulative enclosure could be attached in a matter of seconds, simplifying operations on the laybarge.

Alternately the insulation may be a syntactic foam insulative tape which may wrapped around the pipe and/or joints. The flexible syntactic foam described herein may be extruded into a tape or ribbon form, to one side of which may be applied a self-adhesive coating and/or a release layer which will be removed before installation of the tape. Alternately the tape may be left uncoated, with adhesive being applied to either the tape or the pipe at a later time. An insulated pipe 27 having such a flexible insulative syntactic foam tape 28 wrapped around it is shown in plan view in FIG. 3.

Syntactic foam of the invention made with thermoplastics such as the HIFAX type mentioned is desirably abrasion-resistant, but there may be instances where an outer protective coating is desirable or necessary. Outer abrasion-resistant coatings which could be applied are, e.g., neoprene; polyethylene; polypropylene; polyurethane; polyvinyl chloride; glass; and abrasion-resistant fabrics such as KEVLAR aromatic nylons. Other coatings, imparting advantageous properties to the syntactic foam, can also be applied if desired.

The thermal conductivity of syntactic foam produced according to the invention is generally no higher than about 0.14W/m-°K. Another property of the inventive syntactic foam is its flexibility, which, when installed on a pipe, enables it to bend with the pipe during laying operations. Syntactic foam made in accordance with the invention generally has a flexural modulus of about 3000 to 4000psi, and preferably 3500 to 4000psi.

EXAMPLE

A insulative syntactic foam tape was made in the following manner. The polymer used was a HIFAX (Himont) thermoplastic olefin similar to grade CA10A. Glass microspheres having an average density of 0.28g/cc, an average size of 40μ and an average strength of no more than 20% breakage at 6.89MpA were used.

A two-stage corotating twin screw extruder was used to produce the syntactic foam insulation. The twin screw was assembled of various elements to accomplish each extrusion processing requirement. The barrel temperature was set at 190°C and the twin screw speed was set at 150 RPM. Polymer was fed to the feed section at 45kg/hr. As a homogeneous polymer melt stream was established, microspheres were fed into the second stage at a rate of 6kg/hr. A venting zone built into the second stage was used to effectively remove entrained air from the extrudate. The extrudate reaching the twin-screw tip passed through a die having a rectangular cross-section, resulting in a 25mm wide tape about 6mm thick.

The tape which was produced had a thermal conductivity of 0.135W/m-°K, which is adequate for submarine pipe insulation, and was flexible, abrasion and impact resistant.

It should be noted that the above example and description of the preferred embodiment of the invention are intended to illustrate the invention and not meant to limit on it. It is intended that modifications, variations and changes to the invention may be made within the scope of the appended claims without departing from the spirit and scope of the present invention.

What Is Claimed Is:

1. A method for making syntactic foam insulation, comprising the steps of:
   a) fluidifying a thermoplastic resin to produce a melt stream, said thermoplastic resin having a melt index of from 3 to 30g/10 min;
   b) metering a spherical filler into said melt stream under low shear conditions to form a mixture; and
   c) forming said mixture into a final form.

2. The method of claim 1 wherein said thermoplastic resin is selected from the group consisting of thermoplastic polyolefins; ionically cross-linked thermoplastic polymers derived from ethylene/methacrylic acid copolymers; and polyether blocked polyamide thermoplastic elastomers.

9. The method of claim 1 wherein said thermoplastic resin is selected from the group consisting of polyimides; acrylonitrile-butadiene-styrene resins; acetals; acrylics; cellulosics; chlorinated polyethers; fluorocarbons; nylons; polycarbonates; polyolefins and copolymers thereof; and mixtures thereof.

3. The method of claim 1 wherein the size of said spherical filler is in the range of from about 3 to 100μ in diameter.

4. The method of claim 1 wherein the size of said spherical filler is in the range of from about 5 to 80μ in diameter.

5. The method of claim 1 wherein the size of said spherical filler is in the range of from about 20 to 70μ in diameter.

6. The method of claim 1 wherein the density of said spherical filler is in the range of from about 0.1 to 1.1g/cc.

7. The method of claim 1 wherein the density of said spherical filler is in the range of from about 0.2 to 0.40g/cc.

8. The method of claim 1 wherein unreinforced air is substantially removed from said mixture after said spherical filler is metered into said melt stream under low shear conditions.

9. The method of claim 1 wherein said second stage of said extruder further comprises a venting zone means for substantially removing unreinforced air from said mixture.

10. The method of claim 1 wherein said final form consists of pellets or spheres.

11. The method of claim 10 further comprising the steps of adding said pellets or spheres, as a masterbatch, to an extruder; fluidifying said masterbatch to produce a melt stream; and forming said melt stream into a final form.

12. The method of claim 11 further comprising the step of blending a filler into said masterbatch.

13. The method of claim 12 wherein said filler is selected from the group consisting of rubber and extender resin.

14. The method of claim 1 wherein said final form is a ribbon or tape.

15. The method of claim 1 wherein said melt stream is produced using an extruder.

16. The method of claim 15 wherein said extruder is selected from the group consisting of twin-screw extruders; two-stage extruders; and Buss kneaders.

17. The method of claim 1 wherein a proportion of said spherical filler is metered into a first point of said melt stream under low shear conditions; and the remainder of said spherical filler is metered into a second point of said melt stream, located downstream of said first point, under low shear conditions.

18. The method of claim 1 comprising the additional step of applying an outer coating to said final form.

19. The method of claim 17 wherein said outer coating is selected from the group consisting of neoprene; polyethylene; polypropylene; polyurethane; glass; and aromatic nylons.

20. A method for making an insulated pipe unit comprising superimposing, over the outer surface of a pipe, a covering of syntactic foam pipe insulation made by a process comprising the steps of:
   a) fluidifying a thermoplastic resin to produce a melt stream, said thermoplastic resin having a melt index of from 3 to 30g/10 min;
   b) metering a spherical filler into said melt stream under low shear conditions to form a mixture; and
   c) forming said covering from said mixture.

21. A syntactic foam insulation made by the process comprising the steps of:
   a) fluidifying a thermoplastic resin to produce a melt stream, said thermoplastic resin having a melt index of from 3 to 30g/10 min;
   b) metering a spherical filler into said melt stream under low shear conditions to form a mixture; and
   c) forming said mixture into a final form.

22. The syntactic foam insulation of claim 21 wherein said insulation has a thermal conductivity of no higher than about 0.14W/m-°K.

23. The syntactic foam insulation of claim 21 wherein said insulation has a flexural modulus of at least about 3000 to 4000psi.

24. A syntactic foam insulation comprising:
   a) a thermoplastic resin having a melt index of from 3 to 30g/10 min and being selected from the group consisting of polyolefins and ionically cross-linked thermoplastic polymers derived from ethylene/methacrylic acid copolymers; and
   b) a spherical filler of reinforced air present in an amount of from 10 to 50% by volume of the insulation; and wherein the insulation is substantially free of chain scission agents, has a modulus of elasticity from 3000 to 4000 psi and a thermal conductivity of less than 0.14W/m-°K.

25. The insulation of claim 24 further comprising a second filler selected from the group consisting of rubber and extender resin.

26. The insulation of claim 24 further comprising an outer coating formed on a major surface of the insulation and wherein the coating is selected from the group consisting of neoprene; polyethylene; polypropylene; polyurethane; polyvinyl chloride; glass; and nylon.

27. The syntactic foam insulation of claim 24 wherein the spherical filler is formed of glass microspheres and the size of said spherical filler is in the range of from about 3 to 100μ in diameter.

28. The syntactic foam insulation of claim 24 wherein the density of said spherical filler is in the range of from about 0.1 to 1.1g/cc.

29. An integral insulated pipe section comprising a section of pipe and an outer covering of a syntactic foam pipe insulation comprising: an uncrosslinked thermoplastic resin and from 10 to 50% by volume of the insulation of reinforced air in the form of glass microspheres; wherein the insulation has a thermal conductivity of less than 0.14W/m-°K, a modulus of elasticity from 3000 to 4000 psi, is substantially free of unreinforced air and has less than 5% of the microspheres broken or damaged.

30. The insulated pipe of claim 29 wherein the insulation is applied to the pipe as a tape.

31. The insulated pipe of claim 29 wherein the insulation is applied to the pipe as a molten coating.

32. The insulated pipe of claim 29 wherein the insulation is applied to the pipe as a sleeve.

33. The insulated pipe of claim 29 further comprising a filler selected from the group consisting of rubber and extender resin.

34. The insulated pipe of claim 29 wherein said thermoplastic resin is selected from the group consisting of polyolefins and ionically cross-linked thermoplastic polymers derived from ethylene/methacrylic acid copolymers.

AMENDED CLAIMS

[received by the International Bureau on 6 September 1993 (06.09.93); original claim 9 cancelled; original claim 2 amended; other claims unchanged; (1 page)]

2. (amended once) The method of claim 1 wherein said thermoplastic resin is selected from the group consisting of thermoplastic polyolefins; ionically cross-linked thermoplastic polymers derived from ethylene/methacrylic acid copolymers; [and] polyether blocked polyamide thermoplastic elastomers[.]; polyimides; acrylonitrile-butadiene-styrene resins; acetals; acrylics; cellulosics; chlorinated polyethers; fluorocarbons; nylons; polycarbonates; polyolefins and copolymers thereof; and mixtures thereof.

Please cancel claim 9 (the claim immediately following claim 2).

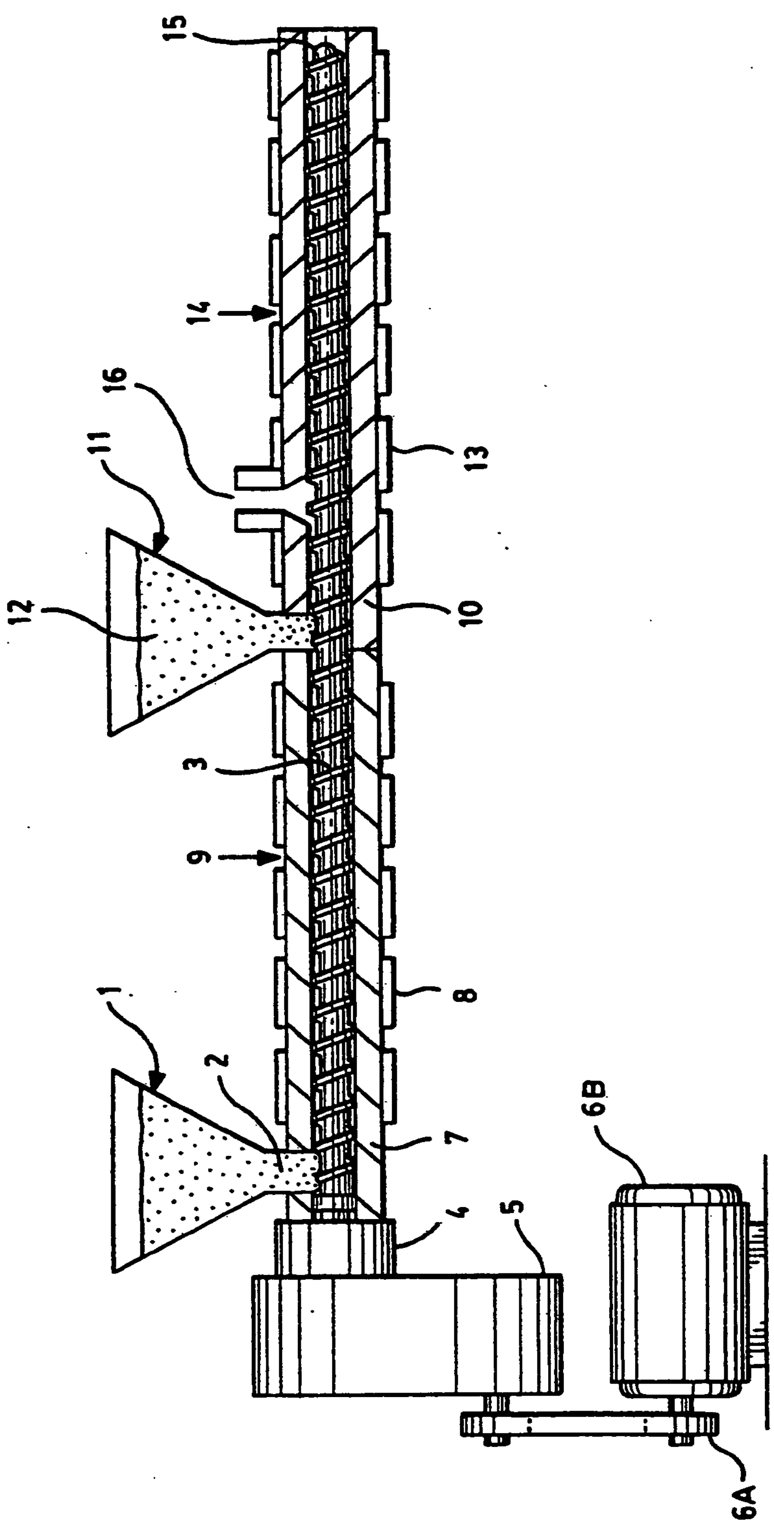

FIG. 1

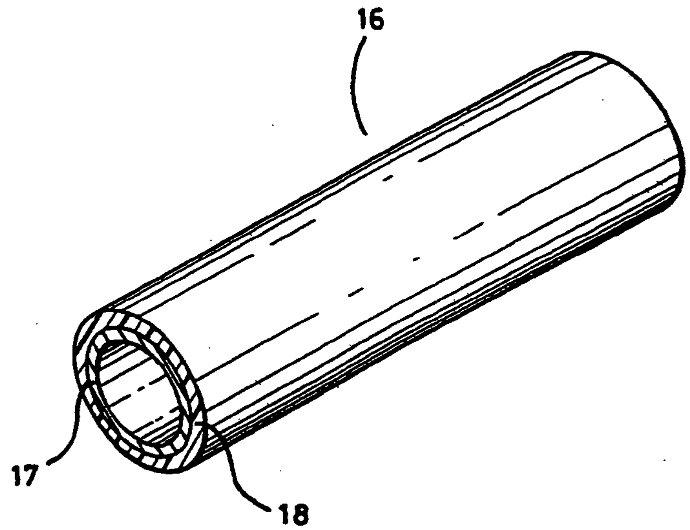

FIG. 2

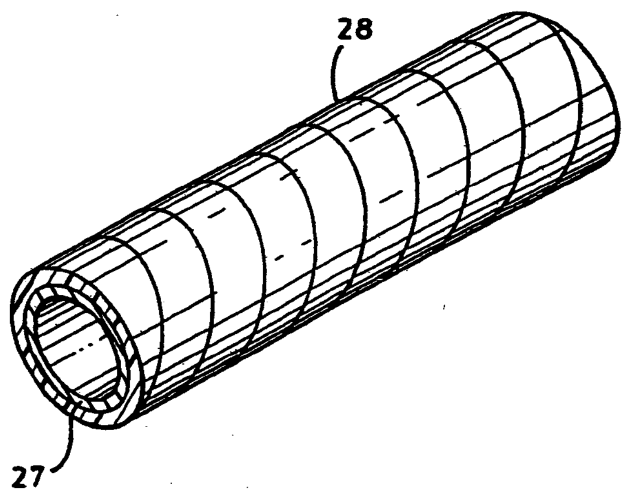

FIG. 3

INTERNATIONAL SEARCH REPORT

PCT/US93/02870

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B29C 67/20; C08J 9/32; F16L 9/14
US CL :264/41; 523/218; 138/145
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/41; 523/218; 138/145 264/DIG.6; 425/812; 138/146,149; 523/219

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 2,884,380 (Cook et al.) 28 April 1959	
Y	US,A, 3,632,256 (Kasting et al.) 04 January 1972 Column 3, line 64- Column 4, line 4.	9
A	US,A, 3,685,804 (Stansfield) 22 August 1972	
A	US,A, 3,807,458 (Royston) 30 April 1974	
Y	US,A, 3,900,543 (Davis) 19 August 1975 Column 5, lines 2-47.	1-20

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search: 24 JUNE 1993

Date of mailing of the international search report: 12 JUL 1993

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Authorized officer
ALLAN KUHNS

Telephone No. (703) 308-3856

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/02870

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,180,536 (Howell, Jr. et al.) 25 December 1979	
A	US,A, 4,273,806 (Stechler) 16 June 1981	
A	US,A, 4,304,704 (Billings) 08 December 1981	
A	US,A, 4,393,901 (Beck) 19 July 1983	
A	US,A, 4,900,488 (Collins et al.) 13 February 1990	
A	US,A, 4,923,538 (Hill) 08 May 1990	
Y	EP,A, 0,473,215 (Coleman-Kammula) 04 March 1992 See the entire document.	1-34
Y,P	US,A, 5,158,727 (Coleman-Kammula et al.) 27 October 1992 See the entire document.	1-34